PATENT SPECIFICATION

795,004

Date of Application and filing Complete Specification Sept. 19, 1955.

No. 26754/55.

Application made in Austria on Sept. 18, 1954.

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Index at acceptance: —Classes 39(3), H2E4H; 82(1), A(8T: 8Z12: 19); and 82(2), U(3: 7L).

International Classification: —C22c. C23f. H05b.

COMPLETE SPECIFICATION

Improvements in or relating to Working Elements, for example Resistance Heating Elements, for use at high temperatures in an atmosphere containing oxygen

We, SIEMENS-PLANIAWERKE AKTIENGESELLSCHAFT, a German company, of Meitingen, near Augsburg, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to working elements, for example resistance heating elements, for use at high temperatures in an atmosphere containing oxygen.

Silicon compounds of the border-line metals of the 4th to 6th group of the Periodic System, and above all molybdenum disilicide, have repeatedly been proposed as materials for use at working temperatures above 1400° C. in an oxidising atmosphere. Thus, this disilicide can be used in conjunction with silicon or other hard materials or oxides as a sintering material or as a protective layer on molybdenum parts.

The surprising resistance to oxidation up to 1700° C. is attributed to the formation of a vitreous covering layer containing SiO_2 upon heat treatment in air. This protective effect also, for example, makes it possible for workpieces formed by powder-metallurgical methods, after having been initially sintered in a reducing atmosphere, to be finally sintered in an oxidising atmosphere, for example, by direct resistance heating of rod-like parts.

It has now been found that the formation of a non-scaling covering layer can only be guaranteed if the oxidation of the molybdenum disilicide takes place at a temperature higher than 700° C. The time until this covering layer is formed depends on the temperature at which formation takes place. The covering layer is formed after about 20 to 50 hours at 750° C. whilst at 1000° C. the covering layer is formed after 5 to 10 hours and after a few minutes at 1400° C. Between 300° and 700° C., and particularly between 500° and 650° C., the molybdenum disilicide is surprisingly destroyed very quickly due to attack by oxygen. Thus, sintered elements were destroyed at 550° C. by a stream of oxygen in a few hours so that they became completely decomposed into a greyish green powder. The destruction apparently commences from the grain boundaries, $MoSi_2$ particles which are enclosed by oxides, being split off. The destruction is not influenced by a higher silicon content, although it is known that this measure improves the non-scaling properties of molybdenum disilicide at temperatures above 700 degrees Centigrade. This unexpected disintegration of molybdenum disilicide in the temperature range indicated occurs in the same way with finally sintered bodies in a hydrogen atmosphere or an inert gas atmosphere. The result is that working elements with varying working temperatures, for example, heating conductors, undergo a very rapid disintegration just in the zones from 300° to 700° C. For example, it could be observed with heating conductors that in the high temperature zone i.e. between 1400 and 1700° C., a fine vitreous covering layer was formed after a short time, while the zone between 300 and 700° C. is subject to a strong action after about 20 to 50 hours, so that the heating rod breaks off at this point due to the reduction in cross-section which occurs and is due to overheating.

According to the present invention there is provided a working element, for example a resistance heating element, for use at high temperatures in an atmosphere containing oxygen, said element being composed, at least in part, of a molybdenum silicon alloy, such as molybdenum disilicide, and having a first zone normally operative at working temperatures of between 1400 and 1700 degrees Centigrade, and a second zone normally operative at working temperatures of between 300 and 700 degrees Centigrade, said second zone

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PATENTS ACT, 1949

SPECIFICATION NO. 795,004

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 30th day of May, 1963 this Specification has been amended under Section 14 in the following manner:-

Page 1, line 32, *after* "parts." *insert* "Such a method and its product form the subject of the claims of Specification No. 791,324, which is of earlier date than the present specification but which was not published prior to the date of the present specification."

Page 1, line 88, Page 2 lines 1 and 2 and lines 56 and 57, *delete* "said second zone having an oxygen impervious coat thereon or being" *insert* "and in which said second zone but not said first zone is either provided with an oxygen impervious coat before the element is subjected to normal operative conditions for the first time or is"

material or as a protective layer on molybdenum parts.

The surprising resistance to oxidation up to 1700° C. is attributed to the formation of a vitreous covering layer containing SiO_2 upon heat treatment in air. This protective effect also, for example, makes it possible for workpieces formed by powder-metallurgical methods, after having been initially sintered in a reducing atmosphere, to be finally sintered in an oxidising atmosphere, for example, by direct resistance heating of rod-like parts.

It has now been found that the formation of a non-scaling covering layer can only be guaranteed if the oxidation of the molybdenum disilicide takes place at a temperature higher than 700° C. The time until this covering layer is formed depends on the temperature at which formation takes place. The covering layer is formed after about 20 to 50 hours at 750° C. whilst at 1000° C. the covering layer is formed after 5 to 10 hours and after a few minutes at 1400° C. Between 300° and 700° C., and particularly between 500° and 650° C., the conductors, undergo a very rapid disintegration just in the zones from 300° to 700° C. For example, it could be observed with heating conductors that in the high temperature zone i.e. between 1400 and 1700° C., a fine vitreous covering layer was formed after a short time, while the zone between 300 and 700° C. is subject to a strong action after about 20 to 50 hours, so that the heating rod breaks off at this point due to the reduction in cross-section which occurs and is due to overheating.

According to the present invention there is provided a working element, for example a resistance heating element, for use at high temperatures in an atmosphere containing oxygen, said element being composed, at least in part, of a molybdenum silicon alloy, such as molybdenum disilicide, and having a first zone normally operative at working temperatures of between 1400 and 1700 degrees Centigrade, and a second zone normally operative at working temperatures of between 300 and 700 degrees Centigrade, said second zone

having an oxygen impervious coat thereon or being of material no part of which is molybdenum silicon alloy.

$MoSi_2$ surfaces are protected in the critical temperature range by the fact that they are covered with a gas-impermeable protective layer consisting mainly of oxides of metals other than molybdenum, for example SiO_2 or Al_2O_3. A very simple and effective protection is obtained if the vitreous covering layer containing SiO_2 is formed on $MoSi_2$ materials. This layer can be formed in an oxygen-containing atmosphere in a manner known *per se* by the parts of the workpieces being heated at temperatures higher than 1300° C., preferably higher than 1350° C., prior to being used at temperatures between 300° and 700° C.

It has also proved satisfactory to cover the $MoSi_2$ surfaces with metallic protective layers applied according to methods known *per se*. For example, good results could be produced with an electrolytically applied chromium layer and with titanium disilicide layer applied by sintering.

Another method of making heating elements of molybdenum disilicide which are resistant to temperatures of above 700° C. and which have zones that are also resistant to oxygen at lower temperatures between 300° C. and 700° C. is to combine a high-temperature part consisting of molybdenum disilicide with a metal part which is resistant to oxidation at such lower temperatures and which is welded on. The following example of the use of this method can be given: A molybdenum disilicide heating conductor for working temperatures up to 1700° C. has metal parts consisting of silver and 5% silicon welded thereon at both ends so as to form the zones of the element which have a working temperature range of between 300° and 700° C. The continuation to the cold copper connection is composed of chromium steel, for example of ferritic chromium steel.

What we claim is:—

1. A working element, for example a rèsistance heating element for use at high temperatures in an atmosphere containing oxygen, said element being composed, at least in part, of a molybdenum silicon alloy, such as molybdenum disilicide, and having a first zone normally operative at working temperatures of between 1400 and 1700 degrees Centigrade, and a second zone normally operative at working temperatures of between 300 and 700 degrees Centigrade, said second zone having an oxygen impervious coat thereon or being of material no part of which is molybdenum silicon alloy.

2. A process for the production of an oxygen impervious vitreous oxide protective layer composed mainly of silicon dioxide upon the second said zone of an element as claimed in Claim 1, said layer being formed by heating said element to a temperature exceeding 1300 degrees Centigrade in an atmosphere containing oxygen.

3. An element as claimed in Claim 1 wherein those parts of the element which are normally operative at temperatures between 300 and 700 degrees Centigrade and which contain molybdenum silicon alloy are covered with a metallic protective layer.

4. An element as claimed in Claim 1, wherein those parts of the element which are normally operative at temperatures between 300 and 700 degrees Centigrade are composed of an oxidation resisting metal, no part of which is molybdenum silicon alloy.

5. A working element, for example a resistance heating element, for use at high temperatures in an atmosphere containing oxygen, substantially as hereinbefore described with reference to the specific example.

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